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**Adsorption of naphthalene from aqueous solution on coal-based  
activated carbon modified by microwave induction: microwave  
power effects**

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**Abstract:** To remove polycyclic aromatic hydrocarbons effectively, coal-based activated carbon (CAC) was produced by various microwave power modification. Original and modified CAC (MCACs) were characterized by N<sub>2</sub> adsorption method, scanning electron microscopy, X-ray photoelectron spectroscopy, Boehm method, and point of zero charge determination. Their adsorption behavior of naphthalene was also investigated. Adsorption equilibrium isotherms, adsorption kinetics, and thermodynamics of naphthalene adsorption on CAC and MCACs were generated. Microwave modification enhanced the basic surface groups of MCACs, extended their Brunauer–Emmett–Teller surface area and pore volume, and varied their distribution of surface oxygen groups. Surface area, pore volume, and functional groups of MCACs were positively related to their naphthalene-adsorption capacity. The adsorption equilibrium of naphthalene on CAC and MCACs needed only 40 min, and this adsorption was fast. Adsorption isotherms revealed that the Freundlich model was applicable to the adsorption process. The adsorption kinetics of naphthalene onto adsorbents was described by pseudo-second-order kinetic model. Naphthalene adsorption was found to a spontaneous and exothermal adsorption process. All these results showed that microwave radiation was an efficient and rapid method of modifying activated carbons. Moreover, MCACs was a promising low-cost and fast adsorbent that can be used to remove naphthalene from aqueous solutions.

**Keywords:** Coal-based activated carbon; microwave; modification; adsorption; naphthalene

## 1. Introduction

The increasing concern over pollution of water courses arising from different anthropogenic activities has resulted in growing demand of activated carbons. They have proved to be effective for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media or from gaseous environments [1]. However, activated carbon is expensive, which limits its large-scale application [2]. Abundant reserves of coal resources exist in Xinjiang, which has unique advantages in raw materials and has attracted an increasing research interest [3, 4].

The excellent performances of activated carbons is well known to be closely related to the well developed porous structures, large surface area and a wide spectrum of surface functional groups. It is an established fact that the activated carbon surface can display acidic, basic and/or neutral characteristics depending on the presence of surface functional groups [5]. Thus, recently focus has been given on how to modify as well as to characterize the surface functional groups of carbon materials in order to improve or enhance their affinities towards certain contaminants [2, 6, 7].

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of chemicals that contain two or more fused benzene rings. Polycyclic aromatic hydrocarbons are priority pollutants due to their carcinogenic, mutagenic, and toxic properties [8, 9]. PAHs are generally produced as by-products during incomplete combustion of fuel, coal, oil, garbage, wood, organic substances, polymers, etc. Because of their chemical persistence and semi-volatile nature, PAHs can travel long distance in air and water, and are difficult to biodegrade. Once inside the human body, PAHs can easily pass through cell membranes and are readily absorbed into the

cells as they are rich in carbon and are hydrophobic. Some PAHs are capable of interacting with DNA, stimulating mutagenic and carcinogenic responses [10]. The U.S. Environmental Protection Agency lists 16 polycyclic aromatic hydrocarbons (PAHs) as priority pollutants [11]. Thus, developing a suitable and effective modification method for removing PAHs from water is necessary.

In recent years, various techniques have been employed for the removal of PAHs from wastewaters [12-14]. Among them, adsorption processes may be effective for the removal of persistent organic pollutants, in particular, activated carbons have been widely used [9, 10,13]. The advantages of the adsorption process are simplicity in operation, inexpensive compared to other separation methods and insensitivity to toxic substances.

Surface modification is frequently applied on ordinary sorbent through incorporating special functional groups onto the sorbent matrix by heating to obtain great sorption capacity and high selectivity for a specific organic compound. Compared with conventional thermal, microwave modification has the advantages of rapid temperature rise, effective effect of surface functionalities and saving of energy method [15]. Menendez et al. [16] found that microwave heating has been used to remove oxygen functionalities and produce a highly-basic activated carbon in just a few minutes, basic properties lasting upon air exposure. Moreover, Nabais et al. [17] and Zhang et al. [18] reported on the surface chemistry modification of carbon materials by means of microwave heating was very effective. Moreover, activated carbon is known to be a good microwave absorber, and modification of activated carbons using microwave radiation is very interesting and valuable.

For these reasons, this work investigated the feasibility of naphthalene adsorption by

microwave radiation modification of coal-based activated carbon (CAC). Surface properties of coal-based activated carbon before and after modification (MCACs) were characterized by means of scanning electron micrograph (SEM), nitrogen adsorption-desorption, Boehm method, point of zero charge ( $\text{pH}_{\text{PZC}}$ ) and XPS. The equilibrium and kinetic data of the adsorption process were then analyzed to study the adsorption isotherms, kinetics, thermodynamics and mechanism of naphthalene from aqueous solution on the CAC and MCACs. An optimal treatment condition was obtained on the basis of the relationship between the physical and chemical properties of the surface and the adsorption capacities of naphthalene. This study developed a modification method for effectively removing hazardous PAHs, particularly naphthalene, and provided a good research idea.

## **2. Materials and Methods**

### *2.1. Preparation of CAC*

The raw material used in this study was anthracite, which was purchased from TBEA, Xinjiang Uygur Autonomous Region, China. The coal was crushed and sieved to 100 meshes. The resultant coal was washed four times with distilled water to remove dust and dried in an air oven at 110 °C for 4 h. CAC was prepared by potassium hydroxide activation in a microwave oven under  $\text{N}_2$  atmosphere. The ration of hydroxide potassium/coal (w/w) was 1:1, microwave power was 700 W, and radiation time was 10 min. After microwave activation, the samples were cooled to room temperature, and washed with 10% hydrochloric acid and then with distilled water repeatedly with distilled water until pH 7 was reached in the residual liquid, dried at 110 °C for 12 h and stored in a desiccator for further use and marked as CAC. All chemicals and reagents used were of analytical grade.

## 2.2. Microwave modification of CAC

Microwave radiation with frequency 2.45 GHz was conducted in microwave reactor (MCR-3) of multi-mode with continuous controllable power. The microwave radiation time was set as 8 min, and different power intervals (300, 500 and 700 W) were chosen to study the modification effects. The modified activated carbons were denoted as MCAC-300W, MCAC-500W and MCAC-700W based on the modification power.

## 2.3. Characterization of CAC and MCACs

### 2.3.1. Textural characterization

Surface properties of original and modified CAC were observed through a scanning electron microscope (SEM, JEOL, JSM-6490LV, Japan) at accelerating voltages of 15 KV. Prior to analysis, samples were dried at 383 K and stored in a desiccator overnight. The SEM enables the direct observation of the changes in the surface microstructures of the carbons due to the modifications.

Elemental analysis of carbon, hydrogen, nitrogen and sulfur was carried out using a VARIOEL III analyzer. The ash content was determined according to proximate analysis of coal and the standard test method for granular activated carbon. The oxygen content was determined by difference.

Surface area and pore size of the samples were measured using a Micromeritics ASAP 2020 surface area analyzer by nitrogen adsorption-desorption method. The samples were degassed under N<sub>2</sub> flow at 350 °C for 6 h before adsorption isotherm were generated by N<sub>2</sub> at 77 K. The surface area ( $S_{BET}$ ) was calculated with the BET equation, the total pore volume ( $V_T$ ) was obtained from the adsorption isotherm at  $P/P_0 = 0.95$ . The micropore area ( $S_{mic}$ ) and



volume ( $V_{mic}$ ) were obtained using the t-plot method. The average pore size ( $r$ ) was estimated by the following equation:

$$r = \frac{4V_T}{S_{BET}} \quad (1)$$

The X-ray photoelectron spectra of CAC and MCAC samples were obtained with a model PHI5700 ESCA X-ray photoelectron spectrometer. XPS was applied to determine the surface complexes on CAC and MCACs. XPS analysis was conducted using Mg Ka X-ray source (1,253.6 eV) under a vacuum pressure  $10^{-6}$  Pa. The wide scans were conducted from 0 to 1000 eV with a pass energy of 50 eV. High-resolution scans of activated carbons were performed over the 524-544 eV range for O 1s with the pass energy of 20 eV.

### 2.3.2. Chemical characterization

The amphoteric characteristics of the treated activated carbon samples were characterized by measuring the amount of the surface functional groups using the acid-base titration method proposed by Boehm [19]. According to this method, 200 mg of each activated carbon sample was added to a series of 100 mL conical flasks containing 25 mL of 0.05 M: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid, respectively. The containers were then sealed and shaken for 24 h at 25 °C, after which the resulting suspensions were filtered and 10 mL of accurately withdrawn aliquot of filtrates were titrated up to pH 4.5 by 0.05 M hydrochloric acid in order to estimate the residual base or up to pH 11.5 by 0.05 M sodium hydroxide for the residual acid. The titration value was measured three times for each sample and then the amount of acidic/basic functional groups was calculated using the average of the three titration data.

The pH at the point of zero charge ( $pH_{PZC}$ ) of the activated carbon, namely the pH value

required to give zero net surface charge. To obtain the  $pH_{PZC}$ , the mixture contained 50.00 mL of 0.01 M NaCl and 300 mg MCAC was agitated for 48 h at  $30 \pm 1$  °C, and the pH of solution was adjusted between 2 and 12 in the process. The pH which adjusted by addition of 0.10 M HCl or NaOH was detected by a pH meter. The  $pH_{PZC}$  is the point where  $pH_{initial} - pH_{final}$  versus  $pH_{initial}$  was 0.

#### 2.4. Adsorption studies

As far as we know, PAHs have low solubility in water. The utilization of ethanol as co-solvent was efficient for the solubilization of naphthalene in aqueous medium. The solutions used in the isothermal and kinetic experiments and in the construction of analytical curves were prepared immediately before use, by diluting the stock solution and adjusting the concentration of ethanol to 30% v/v.

In the adsorption isotherms experiments, naphthalene adsorption was conducted by batch mode in conical flasks at 25 °C. For each sample, 15 mg activated carbon and 100 mL of naphthalene solution corresponding to concentrations in the range of 10–50 mg/L were mixed and shaken for 60 min in a thermostat shaker at 90 rpm. Samples were separated by filtration, and naphthalene concentration was measured using a UV-75N spectrophotometer at 219 nm for naphthalene.

The amount of naphthalene adsorbed on the CAC and MCAC at equilibrium,  $q_e$  (mg/g), can be calculated according to Eq. (2),

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of naphthalene respectively,  $V$  is the volume of the aqueous solution (mL) and  $m$  is the weight of the

adsorbent (g).

Kinetic studies were performed following a similar procedure. The initial concentration was set as 30 mg/L, and the samples were separated at different contacting time intervals. The mixture was filtered, and the residual concentration was determined. The amount of naphthalene at time  $t$ ,  $q_t$  (mg/g), was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (3)$$

where  $C_t$  (mg/L) is the liquid-phase concentration of naphthalene at any time,  $t$  (min).

### 2.5. Regeneration of spent carbon

In the experiment, 15 mg of modified CAC (MCAC-500W) was placed into 100 mL of a naphthalene solution with concentration 30 mg/L and agitated at 25 °C in a thermostat shaker at 90 rpm. After equilibration, the spent carbon was removed and immersed in absolute ethanol for 90 min. The carbon was then dried under vacuum at 110 °C for 24 h. Desorption experiment was conducted again, and the cycle was repeated four times. The amount of naphthalene adsorbed at equilibrium,  $q_e$  (mg/g), was calculated each time.

## 3. Results and discussion

### 3.1. Characterization method

#### 3.1.1. Scanning electron micrograph images

The images obtained from SEM analysis basically illustrated the surface morphologies of the CAC and MCACs materials at lower magnifications (1000×). In order to observe the influence of microwave power on the surface morphology, the SEM image is presented in Fig. 1 ((b)-(d)). As demonstrated in Fig. 1(a), the surface of the unmodified CAC surface exhibits an uneven and rough surface morphology. Chen et.al also observed the phenomenon on

activated carbon derived from pyrolusite-modified sewage sludge [20].

There is little difference in the surface morphology of the samples except for some pore widening on MCAC which could have occurred from the modification process. Apparently the surface of MCAC has more porous structure. Moreover, Foo and Hameed reported the microwave irradiated sample exhibits an even, homogeneous, highly porous and well pronounced array of honey-combed structures [21]. For MCAC-700W, there was happened some collapse in some pores, which could be explained that carbon was calcined with the power increase leading to the temperature rise [18]. Considerable change in pores and morphology are present in MCACs surface, which may benefit for adsorbing PAHs from aqueous solution.

**Fig. 1 should be positioned here.**

### *3.1.2. Elemental analysis*

The elemental composition and chemical properties of CAC and MCAC samples are listed in Table 1. As suggested by the result, compared with the CAC, the carbon content of MCACs increased while the content oxygen of that decreased, which led to the ratio of C/O increase from 2.59 to 4.85. Meanwhile, the content of nitrogen and sulfur also had a certain decrease. However, different microwave power treatments did not produce any further on important change of ash.

**Table 1 should be positioned here.**

### *3.1.3. Brunauer–Emmett–Teller (BET) analysis*

Nitrogen adsorption-desorption isotherms were determined on the samples both before and after modified treatments are shown in Fig. 2. The adsorption isotherms demonstrated a

sharp rise at low  $P/P_0$  range, and a gradual increase was seen at relatively high  $P/P_0$  range. These isotherms clearly show the largely microporous nature of the carbons, with some mesopores leading to a gradual increase in adsorption after the initial filling of the micropores, followed by a more rapid increase near saturation [22]. The saturated adsorption amount of  $N_2$  increased after microwave modification, which implied an increase in the pore volume. For microwave treatment samples, the saturated adsorption amount of  $N_2$  was as follows:  $CAC < MCAC-300W < MCAC-700W < MCAC-500W$ .

The textural characteristics of the CAC and MCAC samples are summarized in Table 1. By comparing the pore characteristics of the samples, it is clear that the microwave modification treatments used in this study caused significant effect on the textural properties [23]. Table 2 shows that BET surface area, Langmuir surface area, and total pore volume of modified samples were greatly improved, all of which imply pore development during the modification process. The modified sample MCAC-500 W had a well-developed porosity with a surface area of  $1061.95 \text{ m}^2/\text{g}$ . Microwave-modified samples were generally conducive to well-developed pore structure of activated carbon. On the other hand, the total pore volume and external specific surface area values increased with the rise of the microwave power, indicating the continuous enlargement of micropores into larger ones [2]. After the modification process, the average pore size increased to more than 2.26 nm for CAC, which only had a certain increase. However, the contraction of carbon skeleton has the same effects on micropores and mesopores and pores of different width are shrinking, so microwave treatment has little effect on the average pore width [18].

**Fig. 2 should be positioned here.**

**Table 2 should be positioned here.**

### *3.1.4 X-ray photoelectron spectra*

XPS has been shown to be useful for analyzing the surface chemical characteristics of CAC. The survey XPS spectra of various samples are shown in Fig. 3(a). Two main peaks were identified and labeled as C 1s and O 1s of CAC and MCAC. It can be seen that the C content increased to some extent after microwave modification treatment, while the contents of O decreased notably, implying the elimination of the oxygen groups of MCAC during the modification process.

The high-resolution spectra of O 1s was given further analysis using a curve-fitting procedure, based on the Gaussian-Lorentzian function after baseline subtraction using Shirley's method. Fig. 3((b)-(e)) showed that the main peaks were identified and labeled as O 1s. Information concerning the components, the peak position and their concentrations were summarized in Table 3. Deconvolution of the O 1s spectra for the CAC and MCAC produced four peaks at 531.2, 532.4, 533.3, and 534.3 eV; these peaks represented O=C, O-C, R-O-C=O, and C-OOH, respectively [24]. In an unmodified CAC, the oxygen functional groups were attributed to a chemical activation process [24]. The ratios of the oxygen functional groups varied with microwave power treatment conditions. For oxygen species, the analysis suggested a decrease in C=O group and an increase in C-O group for the modified carbons, which was consistent with C 1s spectra analysis. The number of R-O\*-C=O functional groups on the microwave-treated samples was lower than that on the raw CAC sample, and a decrease in COOH was observed. These results were consistent with the results of acid-base titration analysis. Apart from thermal decomposition of the acidic groups, the

content of the surface groups also depended on the formation of new groups after modification [2]. Therefore, the modified samples had less acidic groups. According to Menendez et al. [23], thermal treatment can create highly reactive carbon atoms at the crystallite edges, and the re-exposure of such carbons to air results in oxygen adsorption and the formation of new oxygen groups.

**Fig. 3 should be positioned here.**

**Table 3 should be positioned here.**

### *3.1.5 Surface acidity and basicity, surface functional groups and $pH_{pzc}$ value*

The amounts of acidic functional groups and basicity are determined by Boehm method and the result is shown in Fig. 4. Taking into account that NaOH titrates carboxyl, lactone and phenolic groups,  $Na_2CO_3$  titrates carboxyl and lactone, and  $NaHCO_3$  titrates only carboxyl groups, which can therefore obtain the amount of the different acid groups present on the activated carbons [25]. The modification process influenced the functional groups of activated carbons. The modified carbons exhibited an increase in basicity and a decrease in the amount of surface acidic functional groups. As a consequence, the acidic groups were decomposed and removed in the form of CO or  $CO_2$  under microwave radiation [26]. The greatest surface basicity and lowest acidity were obtained from MCAC-500W samples. Total acid groups in the samples decreased in the following order:  $CAC > MCAC-300W > MCAC-700W > MCAC-500W$ . It has been proposed that the basic nature of activated carbon derives primarily from the delocalized  $\pi$ -electrons on the condensed polyaromatic sheets, which would be reinforced if oxygen is removed from the activated carbon surface [4].

**Fig. 4 should be positioned here.**

The  $\text{pH}_{\text{PZC}}$  is an important property of activated carbons. By definition,  $\text{pH}_{\text{PZC}}$  is the pH at which the net surface charge of an adsorbent is zero. The results of  $\text{pH}_{\text{PZC}}$  titrations for modified samples can be seen in Fig. 5. The  $\text{pH}_{\text{PZC}}$  values were 6.83, 8.59, 9.81, and 9.15 for CAC, MCAC-300W, MCAC-500W, and MCAC-700W, respectively; this result was in accordance with the results of the above acid–base titration results. The modification process changed  $\text{pH}_{\text{PZC}}$  of activated carbon, and MCACs possessed higher  $\text{pH}_{\text{PZC}}$  than CAC, which was an evidence of the presence of basic functional groups. Therefore, acidic functional groups also decreased after modification treatments. Most of the acidic oxygen groups were removed from the carbon surface, which resulted in a significant increase in the carbon pH. Menendez et al. [23] modified an activated carbon by a microwave device in a nitrogen flow observed that only a few minutes was sufficient to reduce the oxygen content and to increase its  $\text{pH}_{\text{PZC}}$ .

**Fig. 5 should be positioned here.**

### *3.2. Adsorption studies*

#### *3.2.1 Adsorption kinetic models*

The kinetics of adsorption describes the rate of adsorbate adsorption on activated carbon and it controls the equilibrium time. The kinetic models of pseudo-first-order (Eq. (4)), pseudo-second-order (Eq. (5)), were applied to study the kinetics of the adsorption process, whereas the intraparticle diffusion model (Eq. (6)) was further tested to determine the diffusion mechanism of the adsorption system.

The pseudo-first-order kinetic rate equation is expressed as:



$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \quad (4)$$

where  $k_1$  is the rate constant of pseudo-first-order sorption (min). The first-order rate constant can be determined from the slope of the linearized pseudo-first-order rate equation.

The pseudo-second-order kinetic rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where  $k_2$  is the rate constant of pseudo-second-order sorption (g/(mg·min)). The second-order rate constant can be determined from the intercept of the linearized pseudo-second-order rate equation.

In the intraparticle diffusion model, the relationship between the adsorption capacity at time  $t$ ,  $q_t$  and  $t^{0.5}$  could be written as:

$$q_t = K_p t^{0.5} + C \quad (6)$$

where  $K_p$  is the intraparticle diffusion constant (mg/(g·min)) and  $C$  is the intercept of the line, which is proportional to the boundary layer thickness.

The adsorption kinetics study was carried out to determine the time required for the adsorption equilibrium to be reached. The kinetic curves obtained in our study are shown in [Fig. 6](#). The original and modified samples showed much similar kinetic behavior for naphthalene adsorption. Removal curves were single, smooth, and continuously leading to saturation. The amount of adsorption increased with an increase in contact time. Adsorption equilibrium was observed at 40 min of contact between adsorbent (CAC and MCACs) and naphthalene, beyond which almost no further increase in the amount of adsorption occurred;

thus, the adsorption process was fast. Yakout et al. [10] and Yuan et al. [27] both found that found that the equilibrium time needed for naphthalene adsorption on activated carbon was almost 24 h. Cabal et al. [28] found that the equilibrium time needed for naphthalene adsorption on activated carbons obtained from bean pods was 72 h. Hence, the adsorption performance of MCACs in this study was excellent in comparison with the works done by previous researchers. The adsorption kinetic curves of MCACs showed a great improvement in capacity for the removal of naphthalene over an untreated CAC. The naphthalene amounts adsorbed on MCAC had the following order: MCAC-500W > MCAC-700W > MCAC-300W (Table 4). The experimental points of the pseudo-second-order kinetic model of naphthalene indicated an extremely high-correlation coefficient ( $R^2 > 0.999$ ). The theoretical  $q_e$  values computed from this model were consistent with the experimental  $q_{exp}$  values. The results showed that pseudo-second-order kinetic model fitted for the adsorption of naphthalene well. According to some authors, the pseudo-second-order model may be related to the occurrence of chemical sorption, which may control the reaction rate [29]. The pseudo-second-order model is reported to be usable in the whole adsorption range, and has been applied successfully in many studies [30]. According to the Weber and Morris model, if a linear curve is obtained and it passes through the origin, then the predominant mechanism for adsorption is diffusion [10]. In this work, the behavior of  $q_t$  versus  $t^{0.5}$  graph had relatively low-correlation coefficients ( $0.613 < R^2 < 0.961$ ) and was initially linear, which indicated that diffusion occurred during the adsorption of naphthalene on CAC and MCACs. However, this process was not the only rate-controlling step.

**Fig. 6 should be positioned here.**

**Table 4 should be positioned here.**

### 3.2.2. Adsorption isotherm models

In order to optimize the adsorption process and to forecast adsorption, Langmuir and Freundlich isotherm models were applied to the equilibrium data. Langmuir model is based on the assumption of a homogeneous adsorbent surface, which can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (7)$$

where  $q_e$  (mg/g) is the amount adsorbed per gram of adsorbent,  $C_e$  (mg/L) is the adsorbate concentration in the liquid phase,  $q_m$  (mg/g) is the maximal adsorption capacity,  $K_L$  (L/mg) is a constant related to the free energy of the adsorption.

Freundlich model is an empirical equation assuming heterogeneous adsorbent surface, which can be written as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (8)$$

where  $K_F$  is the unit capacity factor related to the adsorbent capacity and  $n$  is an empirical parameter representing the heterogeneity of site energies, respectively.

The adsorption isotherms of naphthalene from solution on the CAC and MCAC are depicted in Fig. 7. The similar initial shapes of the isotherms for naphthalene adsorption on both the CAC and MCAC suggest that the adsorption occurred via the similar pathways. Naphthalene adsorption on the carbon samples belong to the L type according to the Giles classification [31]. Therefore, no strong competition of the solvent takes place for the active sites of adsorption. The parameters of the two isotherm models are calculated and summarized in Table 5. In this work, the Langmuir isotherm best fits the experimental data

for lower values of  $C_e$ , indicating that initially adsorption occurs as a monolayer phenomenon. However, this mechanism does not persist under higher concentration ranges, and in these cases the adsorption seems to be a multi-layer process. Yakout et al. [10] also observe this result by using low-cost activated carbon derived from agricultural wastes. In addition, the adsorption equilibrium  $q_e$  on CAC and MCAC samples increased from 12.85 to 180.87 mg/g with an increase in the initial concentration from 5 to 60 mg/L. This observation could be explained by the fact that the mass transfer driving force would become large and result in high naphthalene adsorption when the initial concentration increased, whereas the active vacant sites available on the activated carbon were sufficient to adsorb most of the naphthalene molecules at low initial concentration. MCAC had higher adsorption capacities of naphthalene than the original CAC, and the naphthalene amounts adsorbed on these carbons had the following order: MCAC-500W > MCAC-700W > MCAC-300W > CAC. Thus, a relationship existed between the sample surface area, pore volume, and basic properties and the adsorption capacity for naphthalene. As shown in Table 1, the modification samples had some increase in surface area and pore volume. In sum, minimal total acidic groups and a high surface area on the surface of carbons lead to high adsorption capacity of CAC for naphthalene.

Moreover, the role of the hydrophobic nature of the carbons, along with an enhanced basicity, which contribute to enhanced removal of naphthalene [32]. From Table 4, we can see that the models which best represented the data obtained were the Freundlich model (with higher  $R^2 > 0.999$ ) for naphthalene. And all  $1/n$  values between 0.1 and 1 indicated a strong interaction between adsorbent and naphthalene with a favorable adsorption.

Naphthalene adsorption from wastewaters has been investigated by using different substances [10, 29, 34]. The intensity of adsorption and the Freundlich adsorption constant  $K_F$  calculated for each adsorption system are given in Table 6. Compared with the different substances for naphthalene adsorption, the modified samples in our study had a certain advantage with high adsorption capacity.

**Fig.7 should be positioned here.**

**Table 5 should be positioned here.**

**Table 6 should be positioned here.**

### 3.2.3. Thermodynamic parameters

In engineering practice, the activation energy,  $E_a$ , is obtained from an Arrhenius equation (8):

$$\ln k_2 = \ln A - \frac{E_a}{R} \left( \frac{1}{T} \right) \quad (9)$$

where  $k_2$  is the rate constant of second-order adsorption,  $E_a$  (kJ/mol) is called the activation energy, representing the minimum energy that reactants must have for the reaction to proceed.

Thermodynamic parameters were evaluated to confirm the adsorption nature of CAC and MCAC. The thermodynamic constants, free energy change ( $\Delta G^\circ$ , kJ/mol), enthalpy change ( $\Delta H^\circ$ , kJ/mol) and entropy change ( $\Delta S^\circ$ , J/(K·mol)) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The thermodynamics equations were as following:

$$\Delta G^\circ = -RT \ln K_F \quad (10)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

$$\ln K_F = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (12)$$

where  $K_F$  is the adsorption equilibrium constant in Eq. (8) for naphthalene.

The calculated values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $E_a$  for adsorption of naphthalene on the CAC and MCAC samples are listed in Table 6. The activation energy values during the adsorption processes were calculated. Low activation energies were a characteristic for physisorption, which indicated that the main adsorption process to remove naphthalene was physical adsorption.

The thermodynamics parameters of naphthalene adsorption at 10, 25, and 40 °C are listed in Table 7. The negative  $\Delta G^\circ$  values of CAC and MCACs indicated that the adsorption process was spontaneous. This spontaneity could be explained by the fact that the affinity between naphthalene and MCAC surface weakened with increasing temperature. The removal process for naphthalene was generally favored at a low temperature. The negative value of  $\Delta H^\circ$  indicated an exothermal adsorption process, which was consistent with the results obtained earlier in this study, in which naphthalene adsorption decreased with increasing temperature. Naphthalene adsorption onto CAC was clearly entropically driven [9]. The positive values of  $\Delta S^\circ$  showed the high affinity of the activated carbon for naphthalene and the increasing randomness at the solid-solution interface in the adsorbates and adsorbents during the adsorption process [34]. Thus, the adsorption of naphthalene onto CAC and MCAC samples was a complex process.

**Table 7 should be positioned here.**

### 3.3 Effect of surface physicochemical characteristics on adsorption capacity

The adsorption capacity of the CAC and MCAC samples rely on its surface characteristics, e.g. texture and surface physicochemical properties. Correlation analysis was conducted to study the effect of each factor on naphthalene adsorption. BET surface area

presented a good linear relationship with the naphthalene-adsorption capacity for the tested carbons (Fig. 8(a)). A high surface area will generally result in high naphthalene-adsorption capacity. Among all samples, MCAC-500 W had the highest BET surface area (Table 2), which implied that it had the highest capacity of naphthalene. In addition, MCAC-500 W had a larger pore volume than the original CAC. The other microwave-modified samples had similar result, i.e., they had higher naphthalene adsorption than CAC. From Fig. 8(b), we can see that a decrease in surface oxygen containing groups ( $R^2=0.913$ ) and carbonyl groups ( $R^2=0.997$ ) have significant effects on the adsorption capacity of naphthalene. By correlation of the adsorption capacity of naphthalene and total surface oxygen containing groups in Fig. 8(b) showed that adsorption capacities of carbons decreased with the increase in total surface oxygen-containing groups. MCACs with minimal surface oxygen groups presented high naphthalene adsorption capacities. Thus, a combination of high surface area and low surface oxygen group is desired for MCACs with high naphthalene adsorption capacity. This result is in agreement with previous research on hydrophobic volatile organic compounds adsorption [35] and adsorption of phenanthrene in gaseous phase [36].

The well-developed total pore volume, high surface area, and low oxygen content of MCAC samples made them good adsorbents for naphthalene. To improve activated carbon performance for hydrophobic naphthalene adsorption, pore volume and surface area should be as high as possible, and surface oxygen-containing groups need to be reduced.

**Fig. 8 should be positioned here.**

### 3.4. Regeneration

The results of regeneration studies are shown in Fig. 9. MCAC-500 W still had a high

adsorption capacity, which reached a level of 92.8% of the initial value after four cycles. This result indicated the effectiveness of alcohol treatment for the regeneration of spent carbon. Therefore, alcohol treatment is a good choice for the regeneration of naphthalene-exhausted MCAC-500 W. Shi et al. observed that naphthalene adsorption onto a high-surface-area carbon has high capacity after three cycles by the alcohol treatment for the regeneration of the spent carbon [37].

**Fig. 9 should be positioned here.**

## **4. Conclusion**

The surface chemistry and physical properties of CAC samples play important roles on naphthalene adsorption. Changes in the surface chemistry and physical properties of MCACs were studied to obtain thorough understanding of the microwave modification process using various microwave powers.

The pore volume and average pore size of MCAC samples, which were mainly BET surface area, increased under microwave treatment. The surface acidic groups were eliminated from MCACs, but the basic nature was enhanced, as shown by Boehm titration and X-ray photoelectron spectra. MCACs by microwave radiation could effectively adsorb naphthalene and had high adsorption capacity for naphthalene from aqueous solution. Therefore, the well-developed total pore volume, high surface area, and low oxygen content of MCAC samples made them good adsorbents for naphthalene adsorption.

The adsorption kinetics of naphthalene on CAC and MCAC samples showed similar behavior for all analytes. After 40 min of contact between adsorbent and naphthalene, a tendency of the system to reach equilibrium was observed. The kinetic model of



pseudo-second order best represented the adsorption kinetic data of naphthalene. The adsorption isotherm experimental data were best described by Freundlich isotherm models. Activation energies for the adsorption processes were relatively low and a characteristic for physisorption. The thermodynamic parameters obtained in this study indicated the spontaneous and endothermic nature of the naphthalene adsorption on CAC and MCAC samples.

Microwave radiation was proved to be an efficient and rapid method to modify activated carbons. MCAC was a promising low cost and fast adsorbent to be used to remove naphthalene from aqueous solutions.

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